

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

Mo6856/LeA 33,769

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/019577
To be Assigned

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP00/05413

13 June 2000 (13.06.00)

25 June 1999 (25.06.99)

TITLE OF INVENTION

Method for Copolymerizing Polar and Non-Polar Monomers

APPLICANT(S) FOR DO/EO/US SCHERTL, Peter; HOCH, Martin; ARNDT-ROSENAU, Michael; PYRLIK, Oliver and GUILLEMOT, Maud

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Abstract page

U.S. APPLICATION NO. (if known) **10/019577** INTERNATIONAL APPLICATION NO.
To be Assigned **PCT/EP00/05413**

ATTORNEY'S DOCKET NUMBER
Mo6856/LeA 33,769

21. ☐ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO. \$1040.00

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$890.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ 890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
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Total claims	21 - 20 =	1	x \$18.00	\$ 18.00
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Independent claims	4 - 3 =	1	x \$84.00	\$ 84.00
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MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$
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TOTAL OF ABOVE CALCULATIONS = \$ 103.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2. + \$

SUBTOTAL = \$

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)). \$

TOTAL NATIONAL FEE = \$ 992.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +
40.00

TOTAL FEES ENCLOSED = \$ 1032.00

Amount to be
refunded: \$

charged: \$

- a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 1032.00 to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



00157

PATENT TRADEMARK OFFICE

SIGNATURE

Aron Preis

NAME

29,426

REGISTRATION NUMBER

10/019577
531 Rec'd PCT 21 DEC 2001

PATENT APPLICATION
Mo6856
LeA 33,769

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
PETER SCHERTL ET AL) PCT EP00/05413
SERIAL NUMBER: To be assigned)
FILED: Herewith)
TITLE: METHOD FOR COPOLYMERIZING)
POLAR AND NON-POLAR MONOMERS)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to its examination kindly amend the enclosed translation of the captioned patent application as follows:

"Express Mail" mailing label number EP671474751US
Date of Deposit December 21, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)

Donna J. Veatch

(Signature of person mailing paper or fee)

On page 1, please delete the title of the patent application and insert the following in its stead:

-- Method for Copolymerizing Polar and Non-Polar Monomers --.

Replace page 29, a page containing an abstract, with the enclosed page wherein the abstract of the disclosure reads as follows:

Method for Copolymerizing
Polar and Non-Polar Monomers

Abstract of the Disclosure

A process for producing a copolymer is disclosed. The process entails polymerizing at least one polar monomer and at least one non-polar monomer in the presence of one or more compounds of transition metals of groups 5 to 10 of the Periodic System according to IUPAC 1985, one or more radical-producers, and an optional co-catalyst. The copolymers thus produced are suitable for the preparation of a variety of articles, including adhesives.

IN THE CLAIMS:

Please cancel Claim 12.

Amend as follows:

3. A process according to Claim 1 characterized in that the radical-producer is chosen so that the radical-producer(s) initiate polymerization and do not react in a detrimental fashion with the transition metal compound.

4. A process according to Claim 1 characterized in that one or more transition metal complex cation forming compounds or coordination complex compounds are used as co-catalyst, chosen from the group of strong, neutral Lewis acids, ionic compounds with Lewis acid cations or Broenstedt acid cations and non-coordinating anions.

7. A composition according to Claim 5 characterized in that the radical-producer is a peroxide, a diazo compound or a mixture thereof.

8. A composition according to Claim 5 characterized in that one or more compounds chosen from the group of strong, neutral Lewis acids, ionic compounds with Lewis acid cations or Broenstedt acid cations and non-coordinating anions are used as co-catalysts.

9. A composition according to Claim 5 characterized in that the transition metal compound is chosen so that the transition metal compound, optionally in the presence of a co-catalyst, can reversibly form a complex with a radically growing polymer chain and non-polar monomers can be inserted into the bond formed in this way between transition metal and polymer chain.

10. A method of using the composition according to Claim 5 comprising catalyzing the polymerization of copolymers.

11. Copolymers which have a statistical distribution on the molecular level prepared in a process according to Claim 1.

Add the following:

13. A process for producing a copolymer comprising polymerizing at least one polar monomer and at least one non-polar monomer in the presence of one or more compounds of transition metals of groups 5 to 10 of the Periodic System according to IUPAC 1985 and one or more radical-producers.
14. The process of Claim 13 wherein the polymerizing is in the further presence of one or more co-catalysts.
15. The copolymer prepared by the process of Claim 13.
16. A composition containing one or more transition metal compounds from groups 5-10 of the Periodic System according to IUPAC 1985 and one or more radical-producers.
17. The composition of Claim 16 further containing one or more co-catalysts.
18. The composition of Claim 16 wherein the transition metal a member selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, nickel, ruthenium, rhodium and palladium.
19. The composition of Claim 16 wherein the radical-producer is at least one member selected from the group consisting of peroxide and a diazo compound.
20. The composition of Claim 17 wherein the co-catalyst is selected from the group consisting of strong Lewis acids, neutral Lewis acids, ionic compounds with Lewis acid cations, ionic compounds with Broenstedt acid cations, and non-coordinating anions.
21. A method of using the copolymer of Claim 15 comprising preparing a molded article.
22. A method of using the copolymer of Claim 15 comprising preparing an adhesive.

REMARKS

The present amendment seeks to place the application in better conformance with U.S. practice. A page containing an Abstract of the Disclosure is enclosed. Entry of the amendment is requested.

Respectfully submitted,

By



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VERSION TO SHOW MARKINGS WITH CHANGES MADE

On page 1, the title of the patent application has been amended as follows:

[A process] Method for Copolymerizing Polar and Non-Polar Monomers

The Abstract (page 29) has been amended as follows:

[A process] Method for Copolymerizing Polar and Non-Polar Monomers

Abstract of the Disclosure

A process for producing a copolymer is disclosed. The process entails polymerizing at least one polar monomer and at least one non-polar monomer in the presence of one or more compounds of transition metals of groups 5 to 10 of the Periodic System according to IUPAC 1985, one or more radical-producers, and an optional co-catalyst. The copolymers thus produced are suitable for the preparation of a variety of articles, including adhesives.

~~The invention provides a process for copolymerizing polar and non-polar monomers, a catalyst system suitable for this containing one or more transition metal compounds from groups 5-10 of the Periodic System, one or more radical-producers and optionally one or more co-catalysts, the polymers obtainable therefrom and use of the polymers which can be prepared by the process to produce molded articles of all types.~~

IN THE CLAIMS:

Claim 12 has been cancelled.

Claims 3, 4, 7, 8, 9, 10 and 11 have been amended as follows:

3. (Amended) A process according to [one or more of Claims 1 to 2,] Claim 1 characterized in that the radical-producer is chosen so that the radical-producer(s) initiate polymerization and do not react in a detrimental fashion with the transition metal compound.

4. (Amended) A process according to [one or more of Claims 1 to 3,] Claim 1 characterized in that one or more transition metal complex cation forming compounds or coordination complex compounds are used as co-catalyst, chosen from the group of strong, neutral Lewis acids, ionic compounds with Lewis acid cations or Broenstedt acid cations and non-coordinating anions.

7. (Amended) A composition according to [one of more of Claims 5 to 6,] Claim 5 characterized in that the radical-producer is a peroxide, a diazo compound or a mixture thereof.

8. (Amended) A composition according to [one or more of Claims 5 to 7,] Claim 5 characterized in that one or more compounds chosen from the group of strong, neutral Lewis acids, ionic compounds with Lewis acid cations or Broenstedt acid cations and non-coordinating anions are used as co-catalysts.

9. (Amended) A composition according to [one or more of Claims 5 to 8,] Claim 5 characterized in that the transition metal compound is chosen so that the transition metal compound, optionally in the presence of a co-catalyst, can reversibly form a complex with a radically growing polymer chain and non-polar monomers can be inserted into the bond formed in this way between transition metal and polymer chain.

10. (Amended) [Use of] A method of using the composition according to [one or more of Claims 5 to 8] Claim 5 comprising catalyzing the [as a] polymerization [catalyst] of copolymers.

11. (Amended) Copolymers which have a statistical distribution on the molecular level [and which can be] prepared in a process according to [one or more of Claims 1 to 4] Claim 1.

Claims 13 through 22 have been added as follows:

--13. A process for producing a copolymer comprising polymerizing at least one polar monomer and at least one non-polar monomer in the presence of one or more compounds of transition metals of groups 5 to 10 of the Periodic System according to IUPAC 1985 and one or more radical-producers.

14. The process of Claim 13 wherein the polymerizing is in the further presence of one or more co-catalysts.

15. The copolymer prepared by the process of Claim 13.

16. A composition containing one or more transition metal compounds from groups 5-10 of the Periodic System according to IUPAC 1985 and one or more radical-producers.

17. The composition of Claim 16 further containing one or more co-catalysts.

18. The composition of Claim 16 wherein the transition metal a member selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, nickel, ruthenium, rhodium and palladium.

19. The composition of Claim 16 wherein the radical-producer is at least one member selected from the group consisting of peroxide and a diazo compound.

20. The composition of Claim 17 wherein the co-catalyst is selected from the group consisting of strong Lewis acids, neutral Lewis acids, ionic compounds with Lewis acid cations, ionic compounds with Broenstedt acid cations, and non-coordinating anions.

21. A method of using the copolymer of Claim 15 comprising preparing a molded article.

22. A method of using the copolymer of Claim 15 comprising preparing an adhesive.--

A process for copolymerizing polar and non-polar monomers

5 The invention provides a process for copolymerising polar and non-polar monomers, a catalyst system suitable for this containing one or more transition metal compounds from groups 5-10 of the Periodic System, one or more radical-producers and optionally one or more co-catalysts, the polymers obtainable therefrom and use of the polymers which can be prepared by the process to produce molded articles of all types.

10 The copolymerisation of polar and non-polar monomers by radical polymerisation under high pressure is a known process. By way of example, the preparation of ethylene/acrylate copolymers may be mentioned (M. Buback et al., Macromol. Chem. Phys. 1997, 198, 3627) which proceeds at pressures between 1500 and 2500 bar between 130 and 225°C. Furthermore, ethylene/vinyl acetate copolymers are typically
15 prepared at 2380 bar and 280°C. This high pressure of generally 500 to 3000 bar involves not only technical problems but also economic problems. The manufacture of ethylene/vinyl acetate/CO terpolymers also proceeds in a similar manner. Furthermore, the following may be mentioned here as examples: US 3 264 275, US 3 509 115, US 3 948 850, US 4 217 431, US 4 260 722 and US 4 267 090. Solution
20 polymerizations of ethylene and vinyl acetate are described, for example, in EP-A-374 666, EP-A-341 499 and EP-A-307 755. Further references may be found in M. Busch et al., Macromol. Theory Simul. 1998, 7, 435.

According to the prior art, therefore, only acrylates or their salts, vinyl esters and carbon monoxide are suitable for use as monomers for the manufacture of ethylene copolymers. These are used in high pressure processes or else emulsion polymerisations with radical initiation.

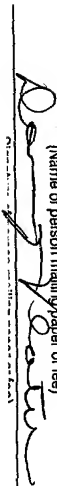
Ethylene/acrylonitrile copolymers have hitherto only been accessible by subsequent hydrogenation of butadiene/acrylonitrile copolymers as described, for example, in DE-A-33 29 974.

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Date of Deposit December 21, 2001

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Donna J. Yeatch

(Name of person mailing paper or fee)



5 The alternating radical copolymerization of acrylic derivatives and ethene at low pressure is known and is described, for example, in DE-A-19 49 370 and in DE-A-44 04 320. The disadvantage of the process described is that copolymerization takes place only in the presence of equimolar, with respect to the polar monomers, amounts of acids or complexing agents and leads only to alternating products and that the removal of these complexing agents after completion of polymerization is achieved only by costly means.

10 WO-A-96/23010 discloses that acrylic ester derivatives or methyl vinyl ketone can be successfully copolymerized using diazadienepalladium complexes. The disadvantages of this process are that polar monomers are incorporated to only a small extent, that the molecular weight of the copolymers obtained is comparatively low even with low rates of incorporation and that comparatively high amounts of catalyst
15 have to be used to prepare the copolymers, which is a problem from an economic point of view.

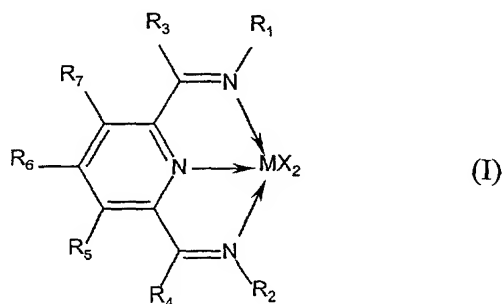
EP-A-558 143 describes a catalyst based on nickel which can be used to copolymerize ethylene and methyl methacrylate. The disadvantage of this process, however, is
20 that again only insufficient amounts of the polar comonomer are incorporated.

WO-A-98/27124 describes a process for polymerizing non-polar monomers (ethylene) using bisiminopyridyl cobalt or iron complexes of the general formula (I) and co-catalysts, and also the support of this type of catalyst systems in the liquid phase
25 or in a fluidised bed process. WO-A-98/30612 describes a process for polymerizing non-polar monomers (propylene) using the catalysts disclosed in WO-A-98/27124. WO-A-99/02472 describes bisiminopyridyl complexes of iron and a process for the oligomerisation and polymerization of ethylene.

30 WO-A-99/12981 describes a catalyst system consisting of bisiminopyridyl complexes of iron, cobalt, ruthenium or manganese for the homopolymerisation and co-

polymerization of ethylene and α -olefins and claims the use of ethene, propene, butene, hexene, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate and styrene. The disadvantage of the process described is that organoaluminum compounds have to be used to activate the bisiminopyridyl complexes and these, as is understood by any person skilled in the art, can react with the claimed polar monomers and thus are then no longer available for activating the catalyst.

G.J.P. Pritovsek et al., Chem. Commun. 1998, 849 describes bisiminopyridyl complexes of iron and cobalt of the general formula (I) and also their use as polymerization catalysts for non-polar monomers.



B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 1998, 120, 4049 and B.L. Small, M. Brookhart, J. Am. Chem. Soc. 1998, 120, 7143 also describe bisiminopyridyl complexes of iron and cobalt of the general formula (I) and their use as polymerization catalysts. Bisiminopyridyl complexes of iron and cobalt of the general formula (I) and their use as polymerization catalysts for propylene are also described in C. Pellecchia, M. Mazzeo, D. Pappalardo, Macromol. Rapid. Commun., 19, 651-55 (1998) and B.L. Small, M. Brookhart, Macromolecules 1999, 32, 2120-30 (1999).

It is a common feature of all the documents that the polymerisations described there are purely coordinative polymerisations and copolymerization with polar molecules does not take place.

There is therefore the object of providing a process for the copolymerization of polar and non-polar monomers and a catalyst system suitable for this purpose.

5 Furthermore, there is the object of avoiding the disadvantages of the copolymerization processes described in the prior art.

10 Thus, the invention provides a process for copolymerizing polar and non-polar monomers, characterized in that at least one polar and at least one non-polar monomer are polymerized in the presence of one or more transition metal compounds from groups 5-10 of the Periodic System according to the IUPAC 1985, one or more radical-producers and optionally one or more co-catalysts.

15 Polar monomers, in the context of the invention, are understood to be radically polymerizable monomers with more or less highly pronounced partial charge distribution within the molecule. Examples of these are chloroprene, styrene, acrylonitrile, vinyl chloride, acrylic acid, acrylates, cyanacrylates, methacrylic acid, methacrylates, acrylamide, methacrylonitrile, vinyl acetate, propene oxide, ethene oxide, vinyl carbazole, vinylpyrrolidone, vinyl esters, and compounds built up from these parent molecules. Acrylonitrile, acrylates, methacrylates and styrene are preferred.

20 Non-polar monomers, in the context of the invention, are understood to be monomers which are polymerizable by coordinative polymerization, without any particular charge separation within the molecule. Examples of these are olefins, in particular ethylene, propylene, butenes, pentenes, hexenes, heptenes, octenes and their higher homologues, diolefins, in particular butadiene, isoprene, pentadienes, hexadienes, heptadienes, octadienes, methyloctadienes, ethylidene norbornene, vinyl norbornene, norbornadienes, cyclooctadienes and their higher homologues and trienes.

25 Obviously the list of suitable polar and non-polar monomers could be extended, but a longer list would certainly not contribute further to understanding the invention.

30

Suitable transition metal compounds, in the context of the invention, are compounds which correspond to the general formula (II),



5

wherein M is a metal from groups 5-10 of the Periodic System according to the IUPAC 1985, preferably a metal selected from the group comprising vanadium, chromium, manganese, iron, cobalt, nickel, ruthenium, rhodium and palladium,

10

wherein L is a 2-, 3- or 4-dentate chelating ligand, preferably a 3-dentate chelating ligand,

wherein Q is a mono-anionic or non-ionic ligand,

15

wherein a and b are each integers with $b \geq 1$, preferably $b \geq 2$ and a is calculated from the (total number of receptor coordination sites on M - b) / the number of donor coordination sites on the ligand.

20

Examples of 2-dentate chelating ligands are diamines such as, for example, ethylene diamine, propylene diamine and butylene diamine, diimines, dipyridyls, dioximes, dioximates, 1,3-diketones such as, for example, acetylacetonate and hexafluoroacetylacetonate, carboxylates, diquinones, semiquinones, bisoxazolines, bithiazolines, 1,10-phenanthroline, 1,8-naphthyridine, pyridyl-2-alkylamines, pyridyl-2-dialkylamines, pyridyl-2-arylamine, pyridyl-2-diarylamine, 2-pyridylimines, pyridine-2-nitriles, dinitriles such as, for example, 1,2-benzodinitrile, 1,8-naphthodinitrile, sulfur diimines, dipyrazolyl borates, dipyrazolyl alkanes, dipyrazolyl ketones, aliphatic and aromatic diphosphines, phosphorimines or phosphorylides.

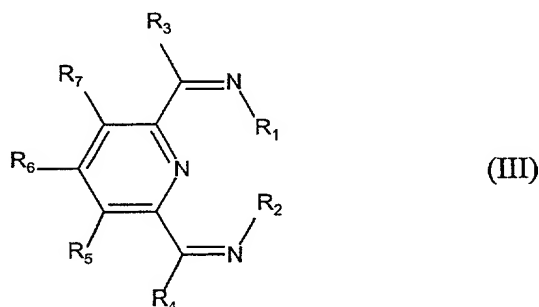
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Preferred 2-dentate chelating ligands are ethylene diamine, propylene diamine, bipyridyl, diimines, 2-pyridylamines, 2-pyridylimines, ethylene diphosphine, 1,3-diphosphinopropane and phosphorylide ligands.

Examples of 3-dentate chelating ligands are terpyridine, triamines, 2,6-diaminopyridyls, 2,6-bisiminopyridyls, 2,6-biscyclopentadienylpyridines, bis-(2,6-hydrazonyl)-pyridines, trispyrazolyl borates, trispyrazolyl alkanes, trispyrazolyl ketones or triphosphines.

Preferred 3-dentate chelating ligands are triamines, trispyrazolyl borates, 2,6-diaminopyridyls, triphosphines and bisiminopyridyl ligands of the general formula (III)



wherein

R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are chosen, independently, from hydrogen, optionally substituted C_1 - C_{10} -alkyl groups, optionally substituted C_6 - C_{14} -aryl groups or are part of a ring system.

Particularly preferably, R^1 and R^2 , independently, represent an optionally substituted aryl group and

R^3 , R^4 , R^5 , R^6 and R^7 are chosen, independently, from hydrogen, optionally substituted C_1 - C_{10} -alkyl groups, optionally substituted C_6 - C_{14} -aryl groups or are part of a ring system.

Examples of 4-dentate chelating ligands are tetraamines, tetrapyridines, tetraphosphines, salen, bis-(pyridylimino)-isoindolines and porphyrins.

Preferred 4-dentate chelating ligands are trialkyltetraamines, triaryltetraamines, tetraphosphines and salen.

5 In general, a list of different 2-, 3- or 4-dentate ligands may be found, for example, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds), Comprehensive Coordination Chemistry - The synthesis, reaction, properties & applications of coordination compounds, Volume 2: Ligands, Pergamon Press, New York, 1st edition 1987, p. 30-56.

10 Examples of mono-ionic and non-ionic ligands Q are halide, hydride, C₁-C₁₀-alkyl or -alkenyl, C₆-C₁₀-cycloalkyl, C₆-C₁₄-aryl, alkylaryl with a C₁-C₁₀-grouping in the alkyl group and a C₆-C₁₄-grouping in the alkyl group, -OR⁸, OR⁸R⁹, -NR¹⁰R¹¹, -NR¹⁰R¹¹R¹², -N(SiR¹⁰R¹¹R¹²)₂, -N(SiR¹⁰R¹¹R¹²)₃, -PR¹⁰R¹¹, PR¹⁰R¹¹R¹², CO, tetrahydrofuran, pyridine, acetonitrile, wherein the Q's may be identical or different, wherein one or more of the two Q groupings may also be bridged and wherein R⁸ to
15 R¹² may be chosen from H, C₁-C₁₀-alkyl, C₃-C₁₀-cycloalkyl, C₆-C₁₄-aryl, alkylaryl or arylalkyl and may be identical or different.

A halogen is understood, by a person skilled in the art, to be fluorine, chlorine, bromine or iodine, preferably chlorine and bromine.

20

C₁-C₁₀-alkyl groups are understood to be all linear or branched alkyl groups with 1 to 10 carbon atoms which are known to a person skilled in the art, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, n-pentyl, i-pentyl, neo-pentyl and hexyl, heptyl, octyl, nonyl and decyl which, for their part, may also be substituted.
25 Suitable substituents here are halogen, nitro, hydroxyl or also a C₁-C₁₀-alkyl, and C₆-C₁₄-cycloalkyl or aryl group, such as benzoyl, trimethylphenyl, ethylphenyl, chloromethyl, chloroethyl and nitromethyl.

C₆-C₁₄-cycloalkyl groups are understood to be all mononuclear or polynuclear cycloalkyl groups with 6 to 14 carbon atoms which are known to a person skilled in the art, such as cyclohexyl, cycloheptyl, cyclooctyl and cyclononyl or also partly or fully
30

hydrogenated fluorenyl which, for their part, may also be substituted. Suitable substituents here are halogen, nitro, C₁-C₁₀-alkoxy or also C₁-C₁₀-alkyl and C₆-C₁₂-cycloalkyl or aryl groups such as methylcyclohexyl, chlorocyclohexyl and nitrocyclohexyl.

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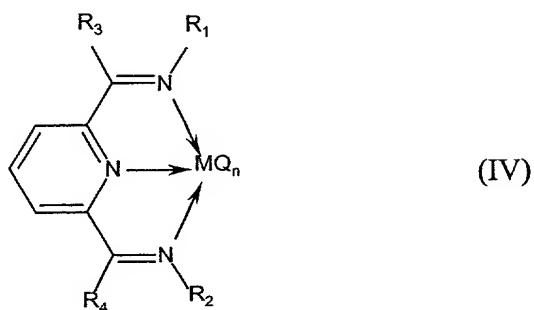
C₆-C₁₄-aryl groups are understood to be all mononuclear or polynuclear aryl groups with 6 to 14 carbon atoms which are known to a person skilled in the art, such as phenyl, naphthyl, fluorenyl which, for their part, may also be substituted. Suitable substituents here are halogen, nitro, C₁-C₁₀-alkoxy or also C₁-C₁₀-alkyl and C₆-C₁₄-cycloalkyl or -aryl groups such as bromophenyl, chlorophenyl, toluyl and nitrophenyl.

10

Q is preferably chosen from halide, in particular chloride and bromide, hydride, methyl, ethyl, butyl, tetrahydrofuran, CO and pyridine.

15

A particularly preferred transition metal compound is represented by the general formula (IV)



20

wherein

M is chosen from iron, cobalt, nickel or palladium,

Q is a mono-anionic or non-ionic ligand, in particular chlorine, methyl, ethyl or hydride,

25

R^1 and R^2 , independently, represent an optionally substituted aryl group, in particular a dialkylphenyl,

5 R^3 and R^4 are chosen, independently, from hydrogen, an optionally substituted C_1 - C_{10} -alkyl group, an optionally substituted C_6 - C_{14} -aryl group or are part of a ring system,

n is 1,2 or 3, in particular 2.

10 The transition metal compound is preferably selected so that the transition metal compound, optionally in the presence of a co-catalyst, can reversibly form a complex with the radically growing polymer chain and non-polar monomers, in particular ole-
fins, can be inserted into the bond formed between transition metal and polymer
15 chain. Without wishing to be firmly committed to this, the applicant's hypothesis is that this insertion takes place via the so-called monometallic mechanism according to Arlman and Coissee in: Journal of Catalysis 1964, 3, 99 et seq. or the bimetallic mechanism according to Patat and Sinn in: Angewandte Chemie 1958, 70, 496.

20 Suitable radical-producers are all radical-producers known to a person skilled in the art which initiate the radical polymerization of polar monomers and simultaneously do not react in a detrimental fashion with the transition metal compound.

25 Depending on the monomer combination used, the most suitable radical-producer can be chosen from the many radical-producers available by means of a few preliminary trials. To list all of these would not contribute anything further to the understanding of the invention. A review of radical-producers which are suitable in principle can be found in G. Allen, J.C. Bevington (eds), Comprehensive Polymer Science, Pergamon Press, 1989, 123 et seq., to which express reference is made at this point.

30 Nevertheless, the following examples of suitable radical-producers may be explicitly mentioned: peroxides such as potassium or sodium peroxodisulfate, dibenzoyl per-

oxide, dicumyl peroxide, tert.-butylcumyl peroxide, cumyl hydroperoxide, tert.-butyl hydroperoxide, di-tert.-butyl peroxide, diisobutyryl peroxide, dilauryl peroxide, didecanoyl peroxide, diisopropyl peroxydicarbonate, dibutyl peroxydicarbonate, tert.-butyl peroxyisopropylcarbonate, tert.-butyl peroxy-pivalate, tert.-amyl peroxy-pivalate, tert.-butyl peroxyisononate, tert.-butyl peroxydiethylacetate or tert.-butyl peroxyacetate and diazo compounds such as 2,2'-azo-bis-(isobutyronitrile), 2,2'-azo-bis-(2-valeronitrile), 1,1'-azo-bis-(1-cyclohexanenitrile) or 4,4'-azo-bis-(4-cyanovale-
5 ric acid), or mixtures of these.

10 The choice of suitable radical-producer depends on the reaction medium and polymerization temperature. To summarize, it may once again be stressed that the radical-producer is chosen so that it initiates radical polymerization of the polar monomer under the given conditions (temperature, pressure, type of monomer, any solvent present, etc.) and at the same time does not react in a detrimental fashion with the
15 transition metal compound or the active transition metal species formed therefrom. For this reason molecular oxygen, for example, is not generally suitable as a radical-producer.

20 In the case of strongly coordinating ligands Q, such as halogen or hydride or even alkylene, it may be necessary to use a co-catalyst in order to replace ligands Q in the transition metal compound with so-called non-coordinating or weakly coordinating ligands. Express reference is made at this point to W. Beck et al., Chemical Reviews 1988, 88, 1405 and S. Strauss, Chemical reviews 1993, 93, 927.

25 In this case, coordination complex compounds may be used as co-catalysts, these being chosen from the group comprising strong, neutral Lewis acids, ionic compounds with Lewis acid cations or Broenstedt acid cations and non-coordinating anions.

30 Strong, neutral Lewis acids which can form stable salts of coordination complexes with Q are preferably compounds of the general formula V in which

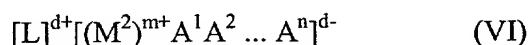


5 M^2 represents an element from group 3 of the periodic table of elements (IUPAC 1985), preferably B, Al or Ga, in particular B,

10 X^1 , X^2 and X^3 represent H, a C_1 - C_{10} -alkyl, C_6 - C_{14} -cycloalkyl, C_6 - C_{14} -aryl group or an alkylaryl, arylalkyl, halogenoalkyl, halogenoaryl, halogenoalkylaryl or halogenoarylalkyl group, each containing C_1 - C_{10} -alkyl, C_6 - C_{14} -cycloalkyl and C_6 - C_{14} -aryl groups and/or fluorine, chlorine, bromine or iodine, in particular halogenoaryl compounds, preferably perfluoro-substituted.

15 In the context of the invention, however, compounds of the general formula (V) in which X^1 , X^2 and X^3 are identical and preferably represent tris-(pentafluorophenyl) borane are particularly preferably used. These compounds and processes for preparing them are known per se and are described, inter alia, in WO-A-93/03067.

20 Compounds of the general formula VI are suitable as ionic compounds with Lewis or Brønstedt acid cations and non-coordinating anions,



wherein

25 L represents a Lewis acid cation in accordance with the Lewis acid/base theory, preferably carbonium, oxonium and/or sulfonium cations and also cationic transition metal complexes, in particular a triphenylmethyl cation, silver cation or ferrocenyl cation, or L represents a Brønstedt acid cation in accordance with the Brønstedt acid/base theory, preferably trialkylammonium, di-
30 alkylaryl ammonium and/or alkyl diaryl ammonium, in particular N,N-dimethylanilinium,

M^2 represents an element from group 3 of the periodic table of the elements (IUPAC 1985), in particular B, Al or Ga, preferably B,

5 A^1 to A^n represent singly negatively charged groups such as hydride, a C_1 - C_{28} -alkyl, C_3 - C_{14} -cycloalkyl, C_6 - C_{14} -aryl group or an alkylaryl, arylalkyl, halogenoalkyl, halogenoaryl, halogenoalkylaryl or halogenoarylalkyl group, each containing a C_1 - C_{28} -alkyl, C_7 - C_{14} -cycloalkyl and C_6 - C_{14} -aryl groups, or a halogen, alkoxide, aryl oxide or organometalloid group, and A_1 to A_n are
10 identical or different,

d is an integer from 1 to 6 and $d = n - m$,

n is an integer from 2 to 8 and

15

m is an integer from 1 to 6.

Preferred anions $[(M^2)^{m+} A^1 A^2 \dots A^n]^{d-}$ in the general formula VI are those in which A^1 to A^n are identical, spatially voluminous, aromatic hydrocarbon groups and M^2 is
20 boron or aluminium, in particular tetraphenyl borate, tetrakis-(3,5-bis-(trifluoromethyl)phenyl) borate and tetrakis-(pentafluorophenyl) borate.

Obviously, mixtures of different compounds of the general formulae (II), (III), (IV), (V) and (VI) and mixtures of different radical-producers and different co-catalysts
25 may also be used.

The radical-producer(s) are generally used at (total) concentrations in the range 0.01 mol.% to 5 mol.%, with respect to the total concentration of polar monomer(s), preferably in the range 0.01 - 1 mol.%. The most appropriate concentration can easily
30 be determined in a few preliminary trials.

The transition metal compound(s) are used in the range 0.005 to 10 mol.%, with respect to the total concentration of radical-producer(s), preferably in the range 0.01 to 0.1 mol.%. The most appropriate concentration can easily be determined in a few preliminary trials.

5

The amount of co-catalyst(s) used depends on the number of ligands Q to be removed from the transition metal compound. Theoretically, one to 1.2 co-catalyst molecules are used per strongly coordinating ligand Q to be removed. This means that, in general, an amount in the range 0.01 to 20 mol.%, with respect to the total concentration of radical-producer(s), preferably in the range 0.01 - 0.5 mol.%, is used.

10

It may be advantageous to apply the catalyst system according to the invention to a support. In this case, bonding should preferably take place via the ligand L so that the components in the catalyst system do not react or interact in a detrimental fashion with the support.

15

Particulate organic or inorganic solids, the pore volumes in which are between 0.1 and 15 ml/g, preferably between 0.25 and 5 ml/g, the specific surface areas of which are greater than 1, preferably 10 to 1000 m²/g (BET), the particle sizes of which are between 10 and 2500 nm, preferably between 50 and 1000 nm, and the surface areas of which can be modified in an appropriate manner are preferably used as support materials.

20

The specific surface area is determined in a conventional manner using Brunauer, Emmet and Teller's method, J. Anorg. Chem. Soc. 1938, 60, 309, the pore volume is determined by McDaniels's centrifuge method, J. Colloid Interface Sci. 1980, 78, 31 and the particle size is determined by Cornillaut's method, Appl. Opt. 1972, 11, 265.

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The following may be mentioned as suitable inorganic solids without, however, intending to restrict the present invention: silica gels, precipitated silicas, clays, alumi-

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nosilicates, talcum, zeolites, carbon blacks, inorganic oxides such as, for example, silicon dioxide, aluminium oxide, magnesium oxide, titanium dioxide, inorganic chlorides such as, for example, magnesium chloride, sodium chloride, lithium chloride, calcium chloride, zinc chloride or calcium carbonate. The inorganic solids mentioned which satisfy the specification mentioned above and are therefore particularly suitable for use as support materials are described in more detail, for example, in Ullmann's Enzyklopaedie der technischen Chemie, vol. 21, p. 439 et seq. (silica gels), vol. 23, p. 311 et seq. (clays), vol. 14, p. 633 et seq. (carbon blacks) and vol. 24, p. 575 et seq. (zeolites).

Powdered polymer materials, preferably in the form of a free-flowing powder, with the properties mentioned above, are suitable as organic solids. The following examples may be mentioned, without intending to restrict the present invention: polyolefins such as, for example, polyethene, polypropene, polystyrene, polystyrene-co-divinylbenzene, polybutadiene, polyethers such as, for example, polyethylene oxide, polyoxytetramethylene or polysulfides such as, for example, poly-p-phenylene sulfide. Particularly suitable materials are polypropylene, polystyrene or polystyrene-co-divinylbenzene. The organic solids mentioned, which comply with the specification mentioned above and are therefore particularly suitable for use as support materials are described in more detail, for example, in Ullmann's Enzyklopaedie der technischen Chemie, vol. 19, p. 195 et seq. (polypropylene) and vol. 19, p. 265 et seq. (polystyrene).

The supported catalyst system may be prepared over a wide temperature range. The process is usually performed at temperatures of -80 to +200°C, preferably -20 to 150°C, in particular 20 to 100°C.

The invention also provides a composition consisting of one or more transition metals from groups 5-10 of the Periodic System according to IUPAC 1985, one or more radical-producers and optionally one or more co-catalysts and its use as a catalyst system in a process for co-polymerization of polar and non-polar monomers.

Polymerization is preferably performed by placing the monomers in contact with the composition according to the invention dissolved in suitable solvents, in the gaseous or liquid phase, finely distributed or suspended in a liquid diluent.

- 5 Other gases or finely distributed liquids may be mixed with the gaseous, liquid or sprayed monomers, these being used for either diluting, spraying or dissipating heat.

- 10 Liquids or liquefied gases which are known to a person skilled in the art and do not have a detrimental effect on polymerization or the catalyst system, in particular saturated hydrocarbons such as pentane, hexane, cyclohexane, petrol and petroleum ether, are suitable as diluents or solvents.

- 15 Polymerization may be performed at pressures of 0.01 bar to 1000 bar, preferably 0.1 to 500 bar, in particular 1 to 100 bar, quite specifically 1 to 10 bar. In general, polymerization is performed at temperatures of -20 to 250°C, preferably 0 to 200°C, in particular 20 to 160°C. As a trivial point, the temperature has to be matched to the radical-producer being used, since the radical-producer also has to decompose at this temperature.

- 20 Since the transition metal compound is generally sensitive to oxygen and water, it is advantageous to exclude oxygen and water.

- 25 The sequence of mixing the individual constituents in the composition may be any order at all. As a rule, the final composition is placed in contact with the monomer mixture and then the temperature is increased to above the decomposition temperature of the radical-producer.

- 30 The invention also provides use of the polymers obtainable in accordance with the invention for preparing molded items of any type, in particular films, sheets, hoses, sections, sheathing, extrudates and injection molded articles. At the molecular level, said polymers are statistical copolymers and not AB-block copolymers. Another pre-

ferred use is use as a starting material for adhesives and additives, in particular oil additives. The composition may be varied over a wide range, depending on the conditions used, the catalytically active composition and the monomer composition and concentration. The molar fraction of polar monomers incorporated to non-polar monomers incorporated is generally in the range 0.05 - 0.95.

5

Polymers prepared according to the invention contain homopolymers of the individual monomers as impurities. For specific applications, it may be advantageous to remove these using appropriate methods, such as fractional precipitation or extraction processes.

10

The following examples are intended to explain the present invention in more detail without, however, restricting this to the examples.

Examples

5 All reactions were performed with the exclusion of air and moisture, if required, and using the variable high vacuum technique. The solvents used were dry, saturated with purified argon and stored under an argon atmosphere.

10 2,2'-azo-bis-(isobutyronitrile), AIBN, is commercially available (Merck KgaA, Germany) and was used without further purification. The potassium perfluorophenyl borate, $K[B(C_6F_5)_4]$, used was prepared from the corresponding lithium compound using S. Cohen and A. Massey's method, Adv. Fluor. Chem. 6, 83-285 (1970), $Na[B(C_6H_5)_4]$ was purchased from Merck KgaA, Germany and used without further purification.

15 The polymerization reactions were performed in a 1 l Buechi glass autoclave at 60°C and the amounts of ethene were determined using a mass flow-meter. The polymers were isolated by precipitating in ethanol, purified by washing with ethanol and dried under vacuum.

20 The concentration of ethene in the polymers was determined using NMR spectroscopy in d_6 -dimethylsulfoxide, the glass transition temperature T_g was determined by DSC and the weight average of the molecular weight M_w and polydispersity M_w/M_n were determined using GPC against a polystyrene standard in dimethylacetamide.

Synthesis of the complexes**2,6-dibenzoylpyridine-bis-(2,6-dimethylphenylimino)-cobalt dichloride
(complex A)****5 Example 1a:****Synthesis of 2,6-dibenzoylpyridine**

10 In a 500 ml round-bottomed flask with a reflux condenser, 32.4 g (243 mmol) of anhydrous aluminium trichloride are added to 20.0 g (98 mmol) of pyridine-2,6-dicarboxylic acid chloride in 250 ml of dry benzene under an Ar atmosphere. The mixture is stirred under reflux for 4 h, then cooled, stirred overnight at room temperature and then again stirred under reflux for 6 h. After cooling, the mixture is carefully poured into 500 ml of ice water. The organic phase is separated and the aqueous phase is washed twice, using 100 ml of diethyl ether each time. The combined organic phases
15 are washed twice, using 100 ml of water each time, and then dried over sodium sulfate. The solvents are removed on a rotary evaporator and the product is recrystallised from diethyl ether. Yield: 16.80 g.

20 ¹H NMR (in acetone-d₆/TMS): δ = 8.32-8.26 (m, 3H), 8.14-8.06 (m, 4H), 7.7-7.4 (m, 6H).

MS: 287, 259, 230, 182, 105, 77, 51

Example 1b**25 Synthesis of 2,6-dibenzoylpyridine-bis-(2,6-dimethylphenylimino)-nickel dibromide**

30 1.20 g (5.5 mmol) of anhydrous nickel dibromide are added to a solution of 1.42 g (5 mmol) of 2,6-dibenzoylpyridine and 1.2 ml (10 mmol) of 2,6-dimethylaniline in 50 ml of glacial acetic acid. The mixture is stirred under reflux for 6 h. An orange-

brown powder precipitates and this is filtered hot. The residue is washed twice, using 50 ml of diethyl ether each time, and dried. Yield: 3.35 g

FT-IR (KBr): $\nu(\text{C}=\text{N}) = 1579 \text{ cm}^{-1}, 1610 \text{ cm}^{-1}$.

5

Example 1c

Synthesis of 2,6-dibenzoyl-bis-(2,6-dimethylphenylimino)-pyridine

10 ml of a 10 % strength aqueous NaCN solution are added to a suspension of 0.71 g (1 mmol) of 2,6-dibenzoylpyridine-bis-(2,6-dimethylphenylimino)-nickel dibromide in 10 ml of THF and stirred at RT for 30 min. The organic phase is separated and dried over sodium sulfate. After removing the solvent, the bis-iminopyridyl derivative remains as a pale yellow powder. Yield: 0.40 g.

15 ^1H NMR (in CDCl_3): $\delta = 8.07$ (m, 1H), 7.77 (m, 2H), 7.43-7.36 (m, 6H), 6.93-6.81 (m, 10H), 2.01 (s, 12H); MS: $M^+ = 494 \text{ g/mol}$.

Example 1d

Synthesis of 2,6-dibenzoylpyridine-bis-(2,6-dimethylphenylimino)-cobalt dichloride

0.07 g (0.5 mmol) of anhydrous cobalt(II) chloride are added to a solution of 0.28 g (0.5 mmol) of 2,6-dibenzoyl-bis-(2,6-dimethylphenylimino)-pyridine in 20 ml of dry THF, at room temperature, and the mixture is stirred at room temperature for 48 hours. Then the solution is evaporated down to one half the volume and 100 ml of hexane is added thereto. The bisiminopyridylcobalt complex precipitates as a pale brown powder and is dried under vacuum after filtration. Yield: 0.15 g.

FT-IR (KBr): $\nu(\text{C}=\text{N}) 1571 \text{ cm}^{-1}$.

30

**2,6-dibenzoylpyridine-bis-(2,6-diisopropylphenylimino)-cobalt dichloride
(complex B)**

Example 2a

5 Synthesis of 2,6-dibenzoyl-bis-(2,6-diisopropylphenylimino)-pyridine

10 A solution of 0.4 ml (3.5 mmol) of titanium tetrachloride in 20 ml of toluene is added dropwise to a solution of 3.6 ml (19 mmol) of 2,6-diisopropylaniline and 0.91 g (3.2 mmol) of 2,6-dibenzoylpyridine, which had been prepared in the same way as described in the example for preparing complex A, in 50 ml of toluene at 0°C. After completion of the addition procedure, the mixture is stirred at room temperature for 90 min and then under reflux for 12 h. After cooling to room temperature, the orange suspension is filtered and the residue is washed three times, using 30 ml of toluene each time. The solvent is distilled off and 100 ml of hexane are added to complete
15 precipitation of the hydrochloride. The mixture is filtered again and the residue is washed free of solvent. Then the residue is recrystallised from methanol. At -18°C, 2,6-dibenzoyl-bis-(2,6-diisopropylphenylimino)-pyridine crystallizes out as a pale yellow solid. Yield: 0.92 g.

20 ¹H NMR (in CDCl₃): δ = 8.05-6.83 (m, 19H), 2.87 (m, 4H), 1.10-0.89 (dd, 24H).

Example 2b

**Synthesis of 2,6-dibenzoylpyridine-bis-(2,6-diisopropylphenylimino)-cobalt(II)
dichloride**

25

0.07 g (0.5 mmol) of anhydrous cobalt(II) chloride are added, at room temperature, to a solution of 0.30 g (0.5 mmol) of 2,6-dibenzoyl-bis-(2,6-diisopropylphenylimino)-pyridine in 30 ml of dry THF and the mixture is stirred at room temperature for 12 h. Then the solution is evaporated down to half the volume and 100 ml of hexane is
30 added thereto. The bisiminopyridylcobalt complex precipitates out as a golden yellow precipitate and is dried under vacuum after filtration. Yield: 0.26 g.

FT-IR (KBr): $\nu(\text{C}=\text{N})$ 1572 cm^{-1} .

Polymerization trials

5

Example 3

Radical polymerization of acrylonitrile (comparison trial)

10 10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced into a 1000 ml glass autoclave. After adding 230 mg (1.4 mmol) of AIBN, the mixture is heated to 65°C and stirred for 4 h at this temperature. Yield: 1.98 g.

Example 4

Polymerization of ethene/AN with [(2,6-iPr₂Ph)₂PhPyr]CoCl₂/K[B(C₆F₅)₄]/AIBN

15

10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced into a 1000 ml glass autoclave. Then 246 mg (1.5 mmol) of AIBN, 11 mg (1.5×10^{-2} mmol) of cobalt compound B and 24 mg (3×10^{-2} mmol) of K[B(C₆F₅)₄] are added, one after the other. The reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the molar ratio of acrylonitrile to ethene is 2:1. Then the mixture is heated to 65°C and polymerized for 4 h at this temperature. Yield: 1.17 g.

20

Example 5

Polymerization of ethene/AN with [(2,6-iPr₂Ph)₂PhPyr]CoCl₂/K[B(C₆F₅)₄]/AIBN

25

5 mg (3×10^{-2} mmol) of AIBN and 10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced and heated to 60°C. Then 22 mg (3×10^{-2} mmol) of cobalt complex B and 47.4 mg (6×10^{-2} mmol) of K[B(C₆F₅)₄] are added. The reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the molar ratio AN:E = 2:1, heated to 65°C and polymerized at this temperature for 24 h. Yield: 0.35 g.

30

Example 6**Polymerization of ethene/AN with [(2,6-iPr₂Ph)₂PhPyr]CoCl₂/K[B(C₆F₅)₄]/AIBN**

- 5 5 ml (75 mmol) of acrylonitrile in 200 ml of toluene are initially introduced. Then
244 mg (1.5 mmol) of AIBN, 11 mg (1.5×10^{-2} mmol) of cobalt complex B and
24 mg (3×10^{-2} mmol) of K[B(C₆F₅)₄] are added, one after the other, at 60°C. The
reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the
molar ratio AN:E = 1:1, heated to 65°C and polymerized at 65°C for 4 h. Yield:
10 0.22 g.

Example 7**Polymerization of ethene/AN with [(2,6-Me₂Ph)₂PhPyr]CoCl₂/K[B(C₆F₅)₄]/AIBN**

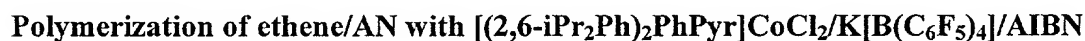
- 15 10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced. Then
246 mg (1.5 mmol) of AIBN, 9.3 mg (1.5×10^{-2} mmol) of cobalt compound A and
24 mg (3×10^{-2} mmol) of K[B(C₆F₅)₄] are added, one after the other, at 60°C. The
reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the
molar ratio AN:E = 2:1, heated to 65°C and polymerized at this temperature for 4 h.
20 Yield: 0.84 g.

Example 8**Polymerization of ethene/AN with [(2,6-Me₂Ph)₂PhPyr]CoCl₂/K[B(C₆F₅)₄]/AIBN**

- 25 5 ml (75 mmol) of acrylonitrile in 200 ml of toluene are initially introduced. Then
245 mg (1.5 mmol) of AIBN, 9.3 mg (1.5×10^{-2} mmol) of cobalt complex A and
24 mg (3×10^{-2} mmol) of K[B(C₆F₅)₄] are added, one after the other, at 60°C. The
reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the
molar ratio AN:E = 1:1, heated to 65°C and polymerized at this temperature for 4 h.
30 Yield: 0.14 g.

Example 9**Polymerization of ethene/AN with**

- 5 10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced. Then 246 mg (1.5 mmol) of AIBN, 11 mg (1.5×10^{-2} mmol) of cobalt compound B and 11.3 mg (3×10^{-5} mmol) of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ are added, one after the other, at 60°C. The reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the molar ratio AN:E = 2:1, heated to 65°C and polymerized at this temperature for 4 h.
- 10 Yield: 0.95 g

Example 10

- 15 10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced. Then 246 mg (1.5 mmol) of AIBN, 11 mg (1.5×10^{-2} mmol) of cobalt compound B and 24 mg (3×10^{-2} mmol) of $\text{K}[\text{B}(\text{C}_6\text{F}_5)_4]$ are added, one after the other, at 60°C. The reactor is sealed and ethene is introduced until the pressure reaches 6 bar, so that the molar ratio AN:E = 1.5:1, heated to 65°C and polymerized at this temperature for 4h.
- 20 Yield: 1.17 g

Example 11**Polymerization of ethene/styrene with**

- 25 5 ml (43 mmol) of styrene in 200 ml of toluene are initially introduced. Then 142 mg (0.9 mmol) of AIBN, 6.3 mg (0.9×10^{-2} mmol) of cobalt compound B and 6 mg (1.8×10^{-2} mmol) of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ are added, one after the other. The reactor is sealed and ethene is introduced until the pressure reaches 2.6 bar, so that the molar ratio styrene:E = 1:1, heated to 65°C and polymerized at this temperature for 4 h.
- 30 Yield: 0.19 g

Example 12**Polymerization of ethene/styrene with**

5

5 ml (43 mmol) of styrene in 200 ml of toluene are initially introduced. Then 180 mg (1.1 mmol) of AIBN, 16 mg (2.2×10^{-2} mmol) of cobalt compound B and 17 mg (4.9×10^{-2} mmol) of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ are added, one after the other. The reactor is sealed and ethene is introduced until the pressure reaches 5.3 bar, so that the molar ratio styrene:E = 1:2, heated to 65°C and polymerized at this temperature for 4 h.

Yield: 0.20 g

Example 13**Polymerization of ethene/MA with**

10 ml (112 mmol) of methyl acrylate in 200 ml of toluene are initially introduced. Then 180 mg (1.1 mmol) of AIBN, 8 mg (1.1×10^{-2} mmol) of cobalt compound B and 8.6 mg (2.5×10^{-2} mmol) of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ are added, one after the other. The reactor is sealed and ethene is introduced until the pressure reaches 3.4 bar, so that the molar ratio MA:E = 2:1, heated to 65°C and polymerized at this temperature for 4 h. Yield: 4.10 g

Example 1425 **Polymerization of ethene/MA with**

5 ml (56 mmol) of methyl acrylate in 200 ml of toluene are initially introduced. Then 180 mg (1.1 mmol) of AIBN, 8 mg (1.1×10^{-2} mmol) of cobalt compound B and 8.6 mg (2.5×10^{-2} mmol) of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ are added, one after the other. The reactor is sealed and ethene is introduced until the pressure reaches 3.4 bar, so that the molar

30

ratio MA:E = 1:1, heated to 65°C and polymerized at this temperature for 4 h. Yield: 1.77 g

Example 15

- 5 **Polymerization of ethene/MA with**
[(2,6-iPr₂Ph)₂PhPyr]CoCl₂/Na[B(C₆H₅)₄]/AIBN

- 10 5 ml (56 mmol) of methyl acrylate in 200 ml of toluene are initially introduced. Then 180 mg (1.1 mmol) of AIBN, 8 mg (1.1×10^{-2} mmol) of cobalt compound B and 8.6 mg (2.5×10^{-2} mmol) of Na[B(C₆H₅)₄] are added, one after the other. The reactor is sealed and ethene is introduced until the pressure reaches 5.1 bar, so that the molar ratio MA:E = 1:1.5, heated to 65°C and polymerized at this temperature for 4 h. Yield: 2.01 g

- 15 **Example 16**

Radical polymerization of methyl acrylate (comparison trial)

- 20 10 ml (112 mmol) of methyl acrylate in 200 ml of toluene are initially introduced into a 1000 ml glass autoclave. After adding 180 mg (1.1 mmol) of AIBN, the mixture is heated to 65°C and stirred at this temperature for 4 h. Yield: 4.72 g.

Overview of results of polymerization trials

Ex. No.	Complex		Borate		AIBN	t _{poly}	Ethene	AN	Styrene	MA	Yield	Ethene in polymer	M _w	M _w /M _n	T _g (2 nd Heat)
	A	B	K(pfb)	Na(pfb)	[mmol]	[h]	[mmol]	[mmol]	[mmol]	[mmol]	[g]	[mol-%]	[g/mol]		[°C]
3	--	--	--	--	1,4	4	--	150	--	--	1,98	0	n.d.	n.d.	109
4	--	0,015	0,030	--	1,5	4	75	150	--	--	1,17	10,3	31370	2,00	87
5	--	0,015	0,030	--	0,03	24	75	150	--	--	0,35	n.d.	n.d.	n.d.	93
6	--	0,015	0,030	--	1,5	4	75	75	--	--	0,22	21,6	9900	1,81	58
7	0,015	--	0,030	--	1,5	4	75	150	--	--	0,84	9,1	21270	1,87	89
8	0,015	--	0,030	--	1,5	4	75	75	--	--	0,14	16,3	8820	1,43	67
9	--	0,015	--	0,030	1,5	4	75	150	--	--	0,95	9,7	23910	2,01	84
10	--	0,015	0,030	--	1,5	4	100	150	--	--	1,17	11,2	24510	1,96	80
11	--	0,009	--	0,018	0,9	4	43	--	43	--	0,19	n.d.	n.d.	n.d.	60
12	--	0,022	--	0,049	1,1	4	86	--	43	--	0,20	n.d.	n.d.	n.d.	58
13	--	0,011	--	0,025	1,1	4	56	--	--	112	4,10	n.d.	n.d.	n.d.	-1,5
14	--	0,011	--	0,025	1,1	4	56	--	--	56	1,77	n.d.	n.d.	n.d.	-3
15	--	0,011	--	0,025	1,1	4	84	--	--	56	2,01	n.d.	n.d.	n.d.	6
16	--	--	--	--	1,1	4	--	--	--	112	4,72	0	n.d.	n.d.	-1

Na(pfb) = Na[B(C₆H₅)₄] and K(pfb) = K[B(C₆F₅)₄]; n.d. = not determined; t_{poly} = polymerization time; AIBN = azobisisobutyronitrile; AN = acrylonitrile;

MA = methyl acrylate; M_w determined via GPC in dimethylacetamide (DMAc) ref. to a poly styrene-standard .

Claims

1. A process for copolymerizing polar and non-polar monomers, characterized in that at least one polar and at least one non-polar monomer are polymerized
5 in the presence of one or more transition metal compounds from groups 5-10 of the Periodic System according to IUPAC 1985, one or more radical-producers and optionally one or more co-catalysts.
2. A process according to Claim 1, characterized in that the transition metal
10 compound is chosen so that the transition metal compound, optionally in the presence of a co-catalyst, reversibly forms a complex with the radically growing polymer chain and non-polar monomers are inserted into the bond thus formed between transition metal and polymer chain.
3. A process according to one or more of Claims 1 to 2, characterized in that the
15 radical-producer is chosen so that the radical-producer(s) initiate polymerization and do not react in a detrimental fashion with the transition metal compound.
4. A process according to one or more of Claims 1 to 3, characterized in that one
20 or more transition metal complex cation forming compounds or coordination complex compounds are used as co-catalyst, chosen from the group of strong, neutral Lewis acids, ionic compounds with Lewis acid cations or Broenstedt acid cations and non-coordinating anions.
- 25 5. A composition containing one or more transition metal compounds from groups 5-10 of the Periodic System according to IUPAC 1985, one or more radical-producers and optionally one or more co-catalysts.

6. A composition according to Claim 5, characterized in that the transition metal is chosen from vanadium, chromium, manganese, iron, cobalt, nickel, ruthenium, rhodium and palladium.
- 5 7. A composition according to one of more of Claims 5 to 6, characterized in that the radical-producer is a peroxide, a diazo compound or a mixture thereof.
- 10 8. A composition according to one or more of Claims 5 to 7, characterized in that one or more compounds chosen from the group of strong, neutral Lewis acids, ionic compounds with Lewis acid cations or Broenstedt acid cations and non-coordinating anions are used as co-catalysts.
- 15 9. A composition according to one or more of Claims 5 to 8, characterized in that the transition metal compound is chosen so that the transition metal compound, optionally in the presence of a co-catalyst, can reversibly form a complex with a radically growing polymer chain and non-polar monomers can be inserted into the bond formed in this way between transition metal and polymer chain.
- 20 10. Use of the composition according to one or more of Claims 5 to 8 as a polymerization catalyst.
- 25 11. Copolymers which have a statistical distribution on the molecular level and which can be prepared in a process according to one or more of Claims 1 to 4.
12. Use of copolymers according to Claim 11 to prepare molded items of all types, adhesives or additives.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

METHOD FOR COPOLYMERIZING POLAR AND NON-POLAR MONOMERS

the specification of which is attached hereto,

or was filed on **June 13, 2000**

as a PCT Application Serial No. **PCT/EP00/05413**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 29 131.4	Germany	June 25, 1999
(Number)	(Country)	(Month/Day/Year Filed)

60/150,634	USA	August 25, 1999
(Number)	(Country)	(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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